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Atmospheric
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Discussions

Interactive comment on “Secondary organic material formed by methylglyoxal in aqueous aerosol mimics – Part 2: Product identification using Aerosol-CIMS” *by* N. Sareen et al.

N. Sareen et al.

vfmcneill@columbia.edu

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We thank Referee 2 for his or her comments. We address the specific points raised by the Referee below.

Specific comments: *1) The DFT calculations of the stability of I- clusters with several of the products are interesting, but they do not aid in the identification of the products. The authors' conclusions and identifications would hold just as well without these calculations. Also, did the authors consider the I- + X → I-.X reaction for cluster formation in addition to the ligand switching channel?*

The DFT calculations were performed because to our knowledge it has not been shown

previously that organic compounds other than organic acids could cluster with I^- for detection via Aerosol CIMS. We did not consider the direct clustering reaction because it is not anticipated to be significant for I^- (Harrison, 1983).

2) In the I- spectrum, the peaks at 225.2 amu and 227.2 amu are identified with a product of molecular formula C6H11O7S+, but a corresponding peak in the H3O+(H2O)n spectrum is not found. This product is shown in Table 1 as containing two carbonyl and one alcohol functional groups which should make it possible to ionize using proton-transfer from the H3O+(H2O)n ions. The fact that these peaks are missing in the positive spectrum calls into question the validity of assigning the 225.2 amu peak in the negative spectrum to the structure proposed in Table 1.

We agree with the reviewer's point; this is why we referred to this assignment as “tentative” in the manuscript. To our knowledge organosulfates have not been previously detected using proton transfer MS.

3) Given the difficulty in assigning peaks in the chemical ionisation mass spectrum with specific products, it seems as if using a complementary method would shed more light on the identity of the products. For example, have the authors considered using electrospray ionisation with a higher-resolution mass spectrometer, perhaps FTMS?

We do not agree with the reviewer that peak assignment is more difficult with Aerosol-CIMS than with other mass spectrometric methods. In fact, the relatively soft chemical ionization method results in little analyte fragmentation and thus simplifies peak identification. The application of the Aerosol-CIMS technique to the study of organic aerosols of known and unknown composition has been validated extensively in the literature (Hearn and Smith, 2004a,b, 2005, 2006a,b, 2007; Hearn et al., 2005, 2007; Renbaum and Smith, 2009a,b; McNeill et al., 2007, 2008) .

4) In Table 1, the molecular formulae are given for the ions detected, but the possible structures correspond to the neutral products (not the ions). This should be corrected.

We have amended the peak assignment tables in response to the reviewer's suggestion.

5) How relevant are pH 2.0 conditions to atmospheric aerosol? Under such acidic conditions, how would nitrogen-containing products be formed? Presumably it would have to involve the reaction of NH4+ ions. Is there any precedence for such a reaction?

The pH studied here is within the range that is relevant to tropospheric aerosols (Keene et al., 2004; Zhang et al., 2007). The mechanism is discussed in detail in the revised manuscript. Two recent studies report the formation of C-N compounds by glyoxal when NH_4^+ is present in the aqueous phase under acidic conditions (Nozière et al., 2009; Galloway et al., 2009), and both propose mechanisms involving ammonia and iminium intermediates. The low pH in this study will result in low equilibrium NH3 concentrations, but the protonation of a carbonyl by NH_4^+ as proposed here and by Nozière et al. (2009) will result in the generation of a short-lived NH3 molecule proximal to the reaction site. Nozière et al. reported that the iminium pathway was active for glyoxal in ammonium-containing solutions down to pH 4.8 (the lowest pH studied).

6) Formation rates for some of the products are estimated, but no attempt is made to relate these to the formation or growth of SOA under atmospheric conditions. Such a calculation would be helpful to illustrate the potential significance of the observed reactions.

A calculation of product formation rates in atmospheric aerosols is included in the revised manuscript.

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